

Interplay between lattice, orbital, and magnetic degrees of freedom in the chain-polymer Cu(II) breathing crystals.

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The chain-polymer Cu(II) “breathing crystals” $C_{21}H_{19}CuF_{12}N_4O_6$ were studied using the X-ray diffraction and *ab initio* band structure calculations. We show that the crystal structure modification at $T=146$ K, associated with the spin crossover transition, induces dramatic changes in the occupation of the Cu e_g sub-shell in half of the Cu sites. This in turn results in the switch of the magnetic interaction sign in accordance with the Goodenough-Kanamori-Andersen theory of the coupling between the orbital and spin degrees of freedom.

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I. INTRODUCTION

The conventional phenomenon of a spin crossover (SCO) is a well-known change of the spin state observed in some octahedral coordinated transition metal complexes. [1] There are exist thermally, doping, photo- and pressure induced SCO transitions. [1–4]. In the classical case of Fe(II) complexes with d^6 electron configuration the thermal SCO involves a transition from the low spin state ($S=0$, t_{2g}^6) to the high spin state ($S=2$, $t_{2g}^4e_g^2$) [5, 6] at elevating temperature. The SCO compounds represent bright examples of a bistability in the molecular crystals[7] and are promising candidates for multifunctional materials[8] with potential applications to the memory devices, the optical, temperature and pressure sensors etc. [9]

Recently rather different SCO transitions were found in the chain-polymer compounds Cu(II) with nitroxides. [10] These compounds contain chains of the exchange clusters with two or three spins. The exchange clusters contain Cu^{2+} , ligands and some organic radicals. For the essential structural changes in the polyhedral surrounding Cu ions under the SCO transitions these compounds were called “breathing crystals”. [11] A classical SCO transition, associated with the change of the spin state of a single ion, is impossible for isolated d^9 centers of Cu(II) ($S=1/2$, $t_{2g}^6e_g^3$). Thus, the reason of unusual spin transitions inherent in the Cu(II) complexes with nitroxides possibly arise from the change of the total electron spin of a whole exchange cluster.

The magnetic measurements show that the temperature induced SCO transition in one of the Cu(II) breathing crystals, characterized by the chemical formula $C_{21}H_{19}CuF_{12}N_4O_6$, is accompanied by the lost of the half of the local spins. [11] This fact can be explained by the formation of the spin singlets ($S=0$) in the half of the

exchange clusters, but the reason for this is unknown.

The aim of our paper is to provide a microscopic description of the changes in the magnetic properties of $C_{21}H_{19}CuF_{12}N_4O_6$, often abbreviated as $Cu(hfac)_2 L^{Me}$ in the chemical literature. With the use of the density functional theory (DFT) we found that there is an interplay between the magnetic properties, orbital structure and lattice distortions in the “breathing crystals”. These correlations between different degrees of freedom results in the SCO transition at 146 K in the compound under consideration.

II. CRYSTAL STRUCTURE

The crystal structure of $C_{21}H_{19}CuF_{12}N_4O_6$ was solved from the X-ray single crystals diffraction data. The data were collected using a SMARTAPEXCCD (Bruker AXS) automated diffractometer with aHelix (Oxford-Cryosystems) open-flow helium cooler using the standard procedure (Mo K α radiation). The structures were solved by direct methods and refined by the full-matrix least-squares procedure anisotropically for non-hydrogen atoms. The H atoms were partially located in difference electron density syntheses, and the others were calculated geometrically and included in the refinement as riding groups. All calculations were fulfilled with the SHELXTL 6.14 program package.

Crystal data for the compound $C_{21}H_{19}CuF_{12}N_4O_6$ at $T = 240$ K are the following: triclinic crystals, space group P-1, $FW = 714.94$, $a = 12.1987(9)\text{\AA}$, $b = 15.5950(11)\text{\AA}$, $c = 15.8716(11)\text{\AA}$, $\alpha = \beta = \gamma = 108.46(1)^\circ$, $V = 2890.1(4)\text{\AA}^3$, $Z = 4$, $D_{calc} = 1.643\text{ g/cm}^3$, $\mu = 0.875\text{ mm}^{-1}$, 12570 measured reflections ($\theta_{max} = 23.35^\circ$), 8291 unique reflections ($R_{int} = 0.0293$), 6043 reflections with $F > 4\sigma(F)$, 793 refined parameters; $GOOF = 1.061$, $R1 = 0.0598$, $wR2 = 0.1500$ ($I > 2\sigma(I)$). Atomic positions for $T=240$ K are presented in the Supplemental materials. [12]

The crystal structure of $C_{21}H_{19}CuF_{12}N_4O_6$ consists of

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TABLE I: The crystal structure data.

Parameters	HT phase	LT phase
T, K	240	110
space group	P-1	P-1
bond/ Å		
Cu-O(1)	2.49	1.99 2.45
Cu-O(2)	1.95-1.96	2.26 1.97
Cu-N	2.30	2.01 2.34

the polymer chains running along b direction (Fig. 1) with a “head-to-head” motif containing the exchange clusters of type $N-\dot{O}-Cu^{2+}$. An isolated chain of the exchange clusters is presented in Fig. 2 with the F and H atoms being omitted for simplicity.

At high temperature (HT) phase the CuO_5N units are the elongated octahedra with Cu-O(1) axial distance of 2.49 Å and Cu-N distance of 2.30 Å. An equatorial distances Cu-O(2) are about 1.95 Å. With decrease of the temperature the compound undergoes the SCO transition in the vicinity of 150 K, which is accompanied by the substantial structural changes. As a result of the transition within a half of the CuO_5N octahedra the lengths of the Cu^{2+} bonds with the axial O and N atoms shorten from 2.49 Å and 2.30 Å to 1.99 Å and 2.01 Å respectively. At the same time two bonds Cu^{2+} with O atoms from equatorial ligands elongate. Within the second half of CuO_5N units the bond length decrease is considerably smaller or they approximately remain the same. [11] Selected parameters of the bond lengths can be found in Tab. I for the HT (240 K) and LT (110 K) phases.

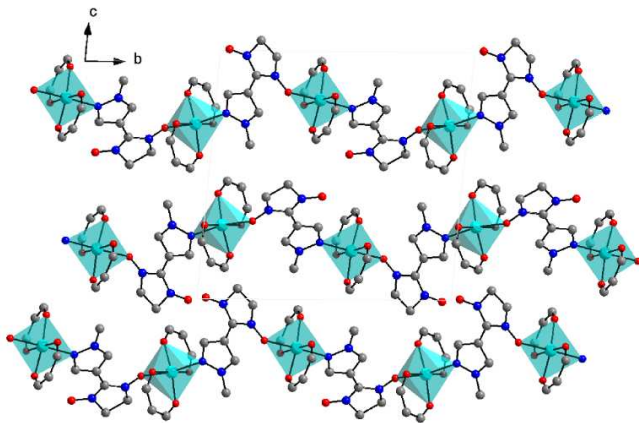


FIG. 1: . (Color online) The crystal structure of the high temperature triclinic phase of the “breathing crystal” compound $C_{21}H_{19}CuF_{12}N_4O_6$. Turquoise balls are the Cu ions, red and blue balls are the O and N atoms. Grey balls are the C atoms. The fluorine atoms and the hydrogen atoms are omitted for clarity of the figure. Coordination units CuO_5N are marked with turquoise octahedra.

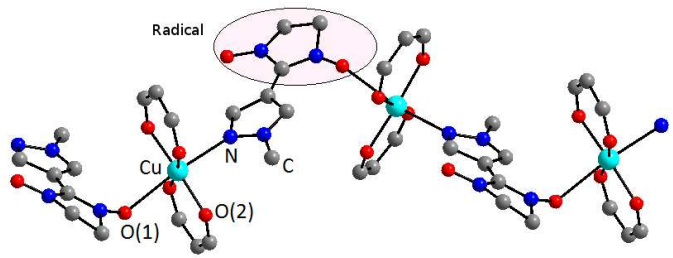


FIG. 2: . (Color online) The structure of isolated polymer chain of the “breathing crystal” compound $C_{21}H_{19}CuF_{12}N_4O_6$. The color coding is the same as in Fig. 1. The fluorine atoms and the hydrogen atoms are omitted for clarity of the figure. Methyl ligand characterizing this compound is marked by C. In other compounds of the “breathing crystals” family the ligand may be propyl or butyl type. A fragment of nitroxide radical with nonzero spin densities on atoms is marked with the oval.

III. PREVIOUS CALCULATIONS OF THE “BREATHING CRYSTALS”

The first attempt to understand a nature of the spin exchange in the clusters containing the Cu atoms and a stable nitroxyl radical was performed rather far ago by Musin et al. [13] The authors provided a detail quantum-chemical analysis of the possible mechanisms of the exchange interaction in the magnetic fragments $\dot{Cu}(II) \cdots O-\dot{N} < (or > \dot{N}-O \cdots Cu(II) \cdots O-\dot{N} <)$ of bischelating complexes of Cu(II) with nitroxyl radicals. The drawback of this and some other [14–17] treatments was in the consideration of an isolated fragment rather than the crystal as a whole.

Till now the only consistent calculation of the electronic and magnetic properties of the “breathing crystals” was performed in Ref. [18], where the spin densities and the magnetic moments of a heterospin compound based Cu(II) hexafluoroacetylacetonate ($Cu(hfac)_2$; $hfac=CF_3-C(O)-CH-C(O)-CF_3$) in combination with a stable nitronyl nitroxide radical were calculated. This system is similar to the one of interest in the present paper, the difference is in another substitute in the position 1 of the pyrazol ring - the ethyl radical instead of the methyl one in our system. This difference results in another organization of the polymer chain: in the case considered in Ref. [18] the chain of the exchange clusters has “head-to-head” coupling of the ligands to the magnetic Cu atoms embedded in $(hfac)_2$ blocks, while in the present case the chain motif is “head-to-tail”.

Thus, in Ref. [18] the corresponding chain contains “three spin - isolated spin” structure, while in the case considered in the present paper the chain is composed of two spin clusters. This results in a different magnetic properties. It should also be mentioned that in Ref. [18] only a high temperature phase of the crystal was calculated. At the same time both high-temperature and especially low temperature phase represent a great interest

for study of phase transitions.

IV. CALCULATION DETAILS

The pseudo-potential PW-SCF code was used for the band structure calculations. [19] We utilized ultrasoft pseudo-potentials with nonlinear core correction (for better description of the magnetic interactions) with Perdew-Burke-Ernzerhof (PBE) version of the exchange-correlation potential. [20] The charge density and kinetic energy cut-offs equal 35 Ry and 180 Ry, respectively. The integration in the k -space in the course of the self-consistency was performed over the mesh of 4 k -points in the Brillouin zone using gaussian smearing of 13.6 meV. The density of states was calculated with the smearing of 40.8 meV.

The correlations on Cu sites were taken into account within the frameworks of the GGA+U approximation (generalized gradient approximation with account of on-site Coulomb repulsion). [21] The intra-atomic exchange interaction J_H and on-site Coulomb repulsion parameters for Cu^{2+} ions were chosen to be 0.9 and 6.1 eV respectively [22, 23].

The calculations were performed for the experimentally measured atomic positions published in Ref. [11] ($T=110$ K) and presented in the Supplemental Materials ($T=240$ K). [12] However, in order to decrease the number of atoms in the unit cell (from 252 to 126) we used P1 instead of the P-1 space group. The inversion center in the P-1 space group produces additional chains, so that reducing the crystal symmetry we neglect the interchain interactions. This seems to be a reasonable approximation, since the main changes in the crystal structures at the SCO transition occur within a chain.

V. CALCULATION RESULTS

A. High-temperature phase

We start with the calculations of the HT phase. Two configurations: ferromagnetic (FM), when both Cu ions in the unit cell (u.c.) have the same spin direction, and antiferromagnetic (AFM), with the opposite spins on the neighboring Cu atoms, were considered.

The magnetic moments on two Cu ions were found to be $0.52 \mu_B$ and $0.55 \mu_B$ (the same for FM and AFM order). They differ from $1 \mu_B$ expected for the isolated Cu^{2+} ions due to a strong hybridization with ligands and formation of a molecular orbital on which a single hole in the $3d$ shell of the Cu^{2+} ion localizes. This molecular orbital (or the Wannier orbital) has the contributions of the Cu d and ligand p orbitals, so that the spin moment on the whole molecular orbitals should be $1 \mu_B$, but the part of the spin density projected on the Cu $3d$ states provides only a half of it.

It is useful to proceed with the analysis of the total magnetization per unit cell defined as $m_{tot} = \sum_i m_i$, where $m_i = g s_i$ is the magnetization on the i th atom, and s_i – its spin moment. The total magnetization equals $3.92 \mu_B$ in the FM and $0.06 \mu_B$ in the AFM configuration. Since there are two pairs radical-Cu in the u.c., it means that at least in the FM configuration the spins on the radicals are *parallel* to the spin moment of the molecular orbital on the neighboring (to this radical) Cu ion. The detailed analysis of the spin density projection on different ions shows that the same is true for the AFM order of the Cu ions. In other words the pair radical-Cu is in the triplet ground state ($S=1$, where S is the spin of the pair). The deviation from the $4 \mu_B$ for the FM and from $0 \mu_B$ for the AFM solutions is attributed to the sparse mesh in the k -space, used to integrate energy bands in such a large unit cell, consisting of 126 atoms.

In principle one may explain the ferromagnetic coupling (parallel spin arrangement) of the spins on the Cu ions and radicals in two ways. First of all one may argue that the local spin on Cu simply magnetizes all the surrounding ions. Microscopically this means that due to a strong hybridization the Zeeman (spin) splitting in the Cu $3d$ shell spreads out on the s and p shells of the neighboring ligands. However, this picture is too simplified and doesn't take into account the details of the electronic structure of the compound under consideration and is unable to explain the antiferromagnetic coupling between Cu and the radical which is observed at low temperatures and will be discussed latter. Therefore below we present the model, which explains in details how the magnetic coupling with the radicals is related to the local lattice distortions and the orbital structure of the Cu– $3d$ shell.

According to the crystal structure analysis presented above in Sec. II the distortions of both CuO_5N octahedra (which belong to the same u.c.) are quite similar. Since the Cu^{2+} ion is Jahn-Teller active, both octahedra are strongly distorted. Actually they are elongated in the direction of O-Cu-N bond. The average Cu-O distance in the equatorial plane is ~ 1.95 - 1.96 Å, while the bond lengths with the apical ligands are 2.30 and 2.49 Å, for the Cu-O and Cu-N bonds respectively.

Such a distortion of the local surrounding of the Cu^{2+} leads to a certain splitting in the e_g shell of these ions: the orbital of the $x^2 - y^2$ symmetry turns out to be higher in energy than $3z^2 - r^2$, as it is shown in Fig. 3a. As a result the hole (electron) with non-compensated spin localizes on this $x^2 - y^2$ molecular orbital, which lies in the plane orthogonal to the bond with the radical.

Thus the overlap between magneto-active orbital centered on the Cu^{2+} ion and the molecular orbital bearing the local spin on the radical is negligible. The only possible magnetic coupling between Cu and the radical is via orbital of the $3z^2 - r^2$ symmetry. But this interaction between the completely filled $3z^2 - r^2$ orbital and the partially filled radical molecular orbital must be ferromagnetic according to famous Goodenough-Kanamori-

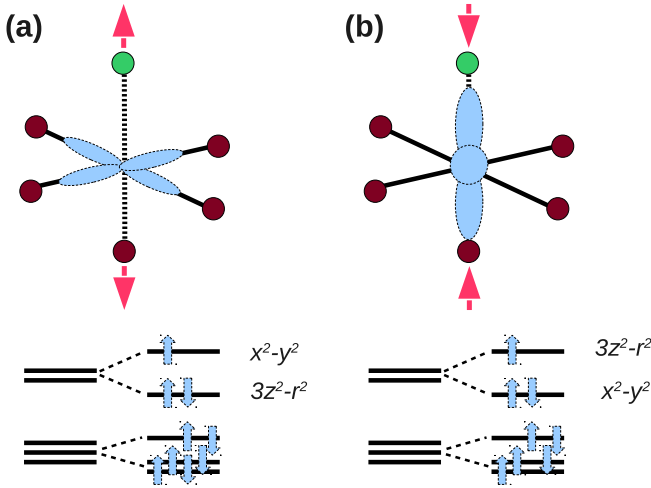


FIG. 3: (Color online) The sketch of the possible local distortions of CuO₅N octahedra (oxygen and nitrogen atoms are brown and green balls, respectively). The direction of the distortion is shown by the red arrows. The elongation (compression) of the octahedra leads to the stabilization of a hole on the $x^2 - y^2$ ($3z^2 - r^2$) orbital as shown in the left (right) panel.

Andersen (GKA) rules. [24] This is exactly what we observe in the calculation.

B. Low-temperature phase

The situation in the low temperature (LT) phase is more complicated, mainly due to different distortions of the octahedra surrounding two Cu²⁺ ions. In contrast to the HT-phase, one of the CuO₅N octahedra turns out to be not elongated, but compressed along one of the bonds. This leads to completely different crystal-field splitting of the Cu 3d shell, such that the orbital of the $3z^2 - r^2$ symmetry appears to be the highest in energy in this octahedra, see Fig. 3b.

The analysis of the occupation matrices obtained in the GGA+U calculations shows that the single hole in the Cu 3d shell indeed localizes on the $x^2 - y^2$ orbital in the elongated (Cu1) and on the $3z^2 - r^2$ orbital of the compressed (Cu2) octahedra (in the HT phase the half-filled orbitals have the $x^2 - y^2$ symmetry on both Cu sites). This is clearly seen in the partial density of states presented in Fig. 4. The magnetic moments were found to be the same in FM and AFM order and equal to $0.46 \mu_B$ and $0.56 \mu_B$ for the Cu1 and Cu2 ions respectively.

In contrast to $x^2 - y^2$, $3z^2 - r^2$ orbital has a direct overlap with the radical molecular orbital bearing non-compensated spin. The overlap between two half-filled orbitals results in the strong antiferromagnetic coupling $J \sim t^2/U$ according to the GKA rules. [24] Here t is

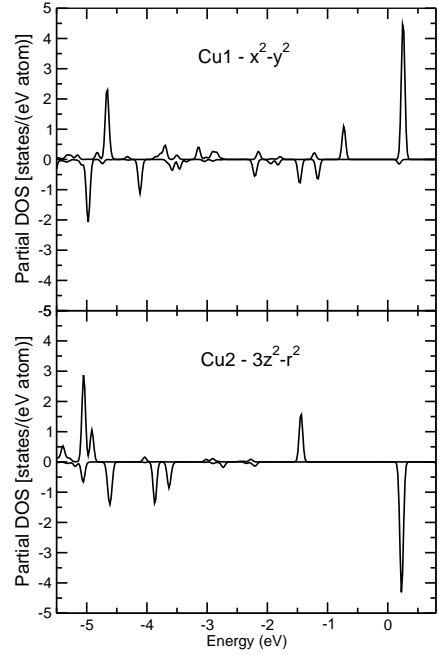


FIG. 4: Results of the GGA+U calculation for the low temperature phase, where the spins on the different Cu ions are antiferromagnetically ordered. Partial density of states for two Cu ions, which belongs to the same unit cell. Cu1 (Cu2) is surrounded by the elongated (compressed) CuO₅N octahedra. Positive (negative) values correspond to the spin up (down). The Fermi energy is set to zero.

the hopping integral and U - on-site Coulomb repulsion parameter.

The total magnetic moment per unit cell is almost the same in the ferromagnetic ($1.97 \mu_B$) and antiferromagnetic ($1.93 \mu_B$) configurations, which shows that there is one pair of electrons on the Cu²⁺ ion and the radical with the parallel spin direction and another one with the antiparallel spins. The fact that the absolute magnetization defined as $m_{abs} = \sum_i |m_i|$ is about $4 \mu_B$ ($3.95 \mu_B$ in both magnetic configurations) additionally supports this interpretation.

The strong antiferromagnetic coupling results in the spin singlet state ($S=0$) formation in the exchange clusters containing the radical and the Cu²⁺ ion placed in the compressed CuO₅N octahedra. This is exactly what is observed experimentally - the loss of the half of the localized spins in the low temperature phase. [11]

VI. SUMMARY

In this paper we present the results of the crystal structure refinement of C₂₁H₁₉CuF₁₂N₄O₆ for T=240 K obtained by the X-ray single crystal diffraction and the the-

ory, which explains the mechanism of the spin crossover transition observed in this compound at $T=146$ K.

With the use of the *ab initio* band structure calculations we show that the change of the local distortions of the CuO_5N octahedra results in the change of the orbital filling with decrease of the temperature. This in turn leads to drastic changes in the magnetic properties. The magnetic coupling in a half of the exchange clusters (consisting of the transitional metal ions and the radicals) changes from ferromagnetic (in the HT phase) to antiferromagnetic (in the LT phase). The strong antiferromagnetic coupling in a half of the exchange clusters results in the spin singlet state formation, so that only a half of the local spins presented in the high-temperature phase are observed in the magnetic measurements at low

temperatures. [11]

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